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Density Functional Study of 8- and 11-Vertex Polyhedral Borane Structures: Comparison with Bare Germanium Clusters

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Density functional theory (DFT) at the hybrid B3LYP level has been applied to the polyhedral boranes $B_nH_n^z$ ($n =$ 8 and 11, $z = -2$, –4, and –6) for comparison with isoelectronic germanium clusters Ge_n^z. The energy differences between the global minima and other higher energy borane structures are much larger relative to the case of the corresponding bare germanium clusters. Furthermore, for both $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$, the lowest energy computed structures are the corresponding experimentally observed most spherical deltahedra predicted by the Wade–Mingos rules, namely the D_{2d} bisdisphenoid and the C_{2v} edge-coalesced icosahedron, respectively. Only in the case of $B_8H_8^{2-}$ is there a second structure close (+2.6 kcal/mol) to the D_{2d} bisdisphenoid global minimum, namely the C_{2v} bicapped trigonal prism corresponding to the "square" intermediate in a single diamond–square–diamond process that can lead to the experimentally observed room temperature fluxionality of $B_8H_8^{2-}$. Stable borane structures with 3-fold symmetry (e.g., D_{3h}, C_{3v}, etc.) are not found for boranes with 8- and 11-vertices, in contrast to the corresponding germanium clusters where stable structures derived from the D_{3d} bicapped octahedron and D_{3h} pentacapped trigonal prism are found for the 8- and 11-vertex systems, respectively. The lowest energy structures found for the electron-rich boranes $B_8H_8^{4-}$ and $B_{11}H_{11}^{4-}$ are nido polyhedra derived from a closo deltahedron by removal of a relatively high degree vertex, as predicted by the Wade–Mingos rules. They relate to isoelectronic species found experimentally, e.g., B_8H_{12} and $R_4C_4B_4H_4$ for $B_8H_8^{4-}$ and $C_2B_9H_{11}^{2-}$ for $B_{11}H_{11}^{4-}$. Three structures were found for $B_{11}H_{11}^{6-}$ with arachno type geometry having two open faces in accord with the Wade–Mingos rules.

1. Introduction

In recent years, our group has used density functional theory (DFT) to study the effects of electron count on the geometry of 6-vertex atom bare clusters of the group 13 elements boron, indium, and thallium[1,2] and five-,[3] six-,[3] seven-,[3] eight-,[4] nine-,[5] and eleven-atom[6] bare germanium clusters. The computed geometries for the five-, six-, seven-, and nine-atom clusters having $2n + 2$ or more skeletal electrons ($n =$ number of vertices) could be rationalized by the Wade–Mingos rules.[7–10] However, for the 8- and 11-vertex bare germanium clusters having $2n + 2$ or more skeletal electrons, a few relatively low energy structures were discovered which did not conform to the Wade–Mingos rules. Such results raised the question as to how closely a bare germanium vertex really mimics an isolobal B–H vertex in a polyhedral borane. To explore this question in more detail, DFT calculations have now been performed on the boranes $B_nH_n^z$ ($n = 8$ and 11, $z = -2$, -4, and -6), using the same computational methods previously used for the germanium clusters. The boranes $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$ studied in this work are also of interest in being the only

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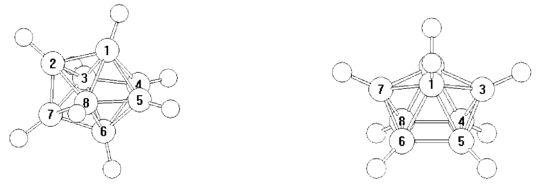
deltahedral borane anions $B_nH_n^{2-}$ ($6 \leq n \leq 12$) exhibiting fluxional mobility at ambient temperatures.[11,12,13]

2. Computational Methods

Geometry optimizations were carried out at the hybrid DFT B3LYP/6-31G(d) level using the Gaussian94 package of programs.[14] Computations were started from the same initial geometries as in the earlier work[4,6] with the germanium clusters. The symmetries were maintained during the geometry optimization processes. In addition, symmetry breaking using modes defined by imaginary frequencies was used to determine optimized structures with minimum energies. Vibrational analyses show that all of the final optimized structures discussed in this paper are genuine minima at the B3LYP/6-31G(d) level without any significant imaginary frequencies ($N_{\mathrm{imag}} = 0$).

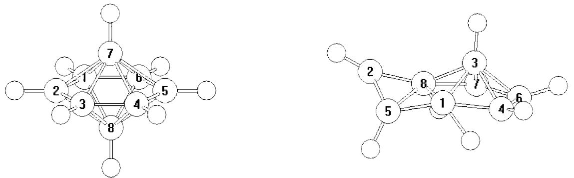
The optimized structures found for the boranes $B_nH_n^z$ ($n = 8$ and 11, $z = -2$ and -4; $n = 11$, $z = -6$) are summarized in Tables 1, 2, 3, 5, and 6 (relative energies in kcal/mol) and Figures 1, 2, 3, 6, and 7. To distinguish between the large number of structures, they are labeled by the number of skeletal electrons and relative energies. Thus, the lowest energy structure with 18 skeletal electrons (i.e., $B_8H_8^{2-}$) is designated as **18-1**. The letter "T" is used to designate triplet structures. Following Williams,[15] the notation ni-n-$\langle R\rangle$ (R = roman numeral) is used to describe a nido structure having all triangular faces except for one larger face with R edges. Replacing "ni" in the above designation by "ar" indicates an arachno structure with two open faces or one large open face. For example, square pyramidal pentaborane B_5H_9 is described as a ni-5-$\langle$IV$\rangle$ structure. More details of all of the optimized structures, including all interatomic distances and the initial geometries leading to a given optimized structure, are provided in the Supporting Information.

3. Results



18-1 (D_{2d}): 0.0 kcal/mole
Bisdisphenoid

18-2 (C_{2v}): + 2.6 kcal/mole
Bicapped trigonal prism



18-3 (D_{6h}): + 15.0 kcal/mole
Hexagonal bipyramid

18-4 (C_1): + 75.4 kcal/mole
Pentagonal pyramid fused to "butterfly"

Figure 1. Four optimized structures computed for $B_8H_8^{2-}$.

Table 1. Optimized Structures for $B_8H_8^{2-}$

structure	rel energy	symmetry	description
18-1	0.0	D_{2d}	bisdisphenoid
18-2	2.6	C_{2v}	ni-8-$\langle$IV$\rangle$ structure (one rectangular face)
18-3	54.7	D_{6h}	hexagonal bipyramid
18-4	75.4	C_1	pentagonal pyramid fused to butterfly

3.1. 8-Vertex Boranes. The $B_8H_8^{2-}$ system (Figure 1 and Table 1) has previously been studied computationally, first by Kleier and Lipscomb[16] and subsequently by Bausch, Prakash, and Williams[17] as well as Bühl, Mebel, Charkin, and Schleyer.[18] The two lowest lying structures found in our work, namely the D_{2d} bisdisphenoid (**18-1**) as the global minimum and a C_{2v}"nido" type bicapped trigonal prism with one rectangular face (**18-2**) at 2.6 kcal/mol above the global minimum, are in essential agreement with the results of these earlier workers. These computations are consistent with the fluxional mobility of D_{2d} bisdisphenoidal $B_8H_8^{2-}$ (**18-1**) through a single diamond−square process involving the C_{2v} nido bicapped trigonal prism **18-2** as the "square" intermediate in accord with experimental data.[11,12]

No other low energy structures were found for $B_8H_8^{2-}$ as genuine local minima (with no imaginary vibrational frequencies). The next higher energy structure for $B_8H_8^{2-}$ was found to be hexagonal bipyramid **18-3** at +54.7 kcal/mol above the global minimum of **18-1**. The hexagonal bipyramid of **18-3** is a deltahedron like the bisdisphenoid of **18-1** but a "less spherical" one, since it has two degree 6 vertices and six degree 4 vertices. A comparison of the energies of **18-1** and **18-3** indicates the importance of having the vertices as equivalent as possible (i.e., as "nearly spherical" as possible) in a stable borane polyhedron without any heteroatoms.

One of the motivations for this computational study was the evaluation of the T_d tetracapped tetrahedron as a possible structure for $B_8H_8^{2-}$, since this structure was found[4] to be the global minimum for the isoelectronic germanium cluster Ge_8^{2-}. However, attempted optimization of a T_d tetracapped tetrahedral structure for $B_8H_8^{2-}$ led ultimately to the same D_{2d} bisdisphenoidal structure (**18-1**) after following all of the modes corresponding to the imaginary frequencies. Therefore, a T_d tetracapped tetrahedron appears to be an unfavorable structure for $B_8H_8^{2-}$, in contrast to the case of Ge_8^{2-}, where it is the global minimum. Another optimization route from a T_d tetracapped tetrahedron in a different sequence along the modes corresponding to the imaginary frequencies led to the unsymmetrical open structure **18-4** at the very high energy of +75.4 kcal/mol above the global minimum of **18-1**. This structure, which can be described as a pentagonal pyramid fused to a "butterfly" by sharing an edge, is likely to be of too high energy and too low symmetry to be of chemical interest.

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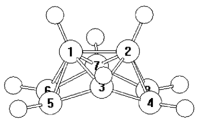
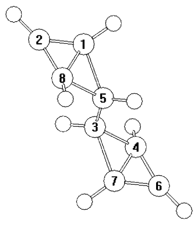
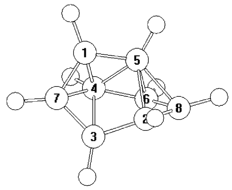


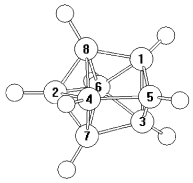
20-1 (**C_{2v}**)**: 0.0 kcal/mole**
ni-8-⟨VI⟩ structure



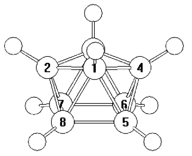
20–2 (**C_{2h}**)**: +24.2 kcal/mole**
Linked "butterflies"



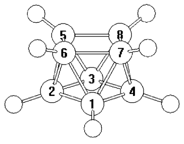
20–3 (**C_2**)**: +41.1 kcal/mole**
3-capped ar-7-⟨IV,V⟩ structure



20–4 (**C_1**)**: +53.1 kcal/mole**
ar-8-⟨IV,IV⟩ structure



20–5(**C_{2v}**)**: +56.2 kcal/mole**
ni-8-⟨IV⟩ structure



20–6T (**D_{4d}**)**: +69.3 kcal/mole**
Square antiprism (triplet)

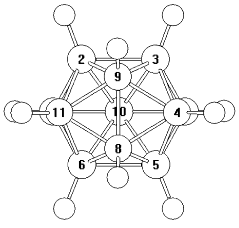
Figure 2. Six optimized structures computed for $B_8H_8^{4-}$.

Table 2. Optimized Structures for $B_8H_8^{4-}$

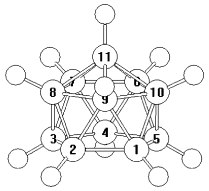
structure	rel energy	symmetry	description
20-1	0.0	C_{2v}	ni-8-⟨VI⟩ structure (one hexagonal face)
20-2	24.2	C_{2h}	two butterflies linked at wing tips
20-3	41.1	C_2	3-capped ar-7-⟨IV,V⟩ structure
20-4	53.1	C_1	ar-8-⟨IV,IV⟩ structure
20-5	56.2	C_{2v}	ni-8-⟨IV⟩ structure (one rectangular face)
20-6T	69.3	D_{4d}	square antiprism (triplet)

The $B_8H_8^{4-}$ anion was first studied computationally by Tebben, Ji, Williams, and Bausch,[19] who found a ni-8-⟨VI⟩ nido structure with a hexagonal open face as the only minimum. In accord with these workers, we find such a structure (**20-1** in Figure 2) to be the global minimum for $B_8H_8^{4-}$. This structure is found experimentally in its tetraprotonated form, namely octaborane-12,[20] B_8H_{12}. In addition, an isoelectronic carborane of the type $R_4B_4C_4H_4$ has this ni-8-⟨VI⟩ structure.[21] Structure **20-1** (Figure 2) is analogous to the global minimum found for Ge_8^{4-} in our previous study.[6]

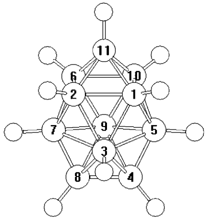
We have also found the following additional higher energy structures for $B_8H_8^{4-}$ (Figure 2 and Table 2), which were not observed by the previous workers:[19] (a) The C_{2h} structure **20-2** at +24.2 kcal/mol above the global minimum of **20-1** can be described as two B_4H_4 butterflies linked by a relatively short B−B bond at the wingtips. (b) The C_2 structure **20-3** at +41.1 kcal/mol is derived from a 7-vertex arachno structure with one quadrilateral and one pentagonal face by capping one of the triangular faces. Since the 7-vertex arachno structure requires $(2)(7) + 6 = 20$ skeletal electrons and since capping the triangular face with a B−H vertex contributes two electrons and no bonding orbitals, structure **20-3** is consistent with the Wade−Mingos rules.[7−10] (c) The C_1 structure **20-4** at +53.1 kcal/mol is an arachno structure with two quadrilateral faces. The low symmetry of this structure indicates that all of its molecular orbitals are nondegenerate, implying that a stable arachno structure is possible with two skeletal electrons less than the $2n + 6$ skeletal electrons required for an arachno structure. (d) The C_{2v} structure **20-5** at 56.2 kcal/mol is a nido structure with one rectangular face very similar to structure **18-2** for $B_8H_8^{2-}$ (Figure 1) discussed above. (e) The triplet D_{4d} square antiprismatic structure **20-6T** is +69.3 kcal/mol above the global minimum of **20-1**. This structure can formally be derived from a hypothetical arachno square antiprism $B_8H_8^{6-}$ by a two-electron oxidation which removes exactly half of the electrons from a doubly degenerate highest occupied molecular orbital, leading to a triplet state. All of these structures have much higher energies than the global minimum of **20-1**.



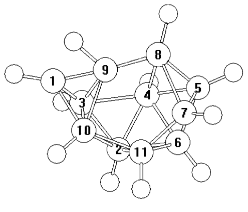
24-1 (**C_{2v}**)**: 0.0 kcal/mole**
Edge-coalesced icosahedron
(**$v_6 = 1$, $v_4 = 2$**)



24-2T (**C_{5v}**)**: +38.0 kcal/mole**
ni-11-⟨V⟩ structure (triplet)



24-3 (**C_{2v}**)**: +43.3 kcal/mole**
Alternative 11-vertex deltahedron
(**$v_6 = 2$, $v_4 = 3$**)



24-4 (**C_1**)**: + 92.5 kcal/mole**
3-capped ni-10-⟨V⟩ structure

Figure 3. Four optimized structures computed for $B_{11}H_{11}^{2-}$.

In accord with the earlier workers,[19] we find no evidence for any ni-8-⟨V⟩ structures (i.e., nido structures with an open pentagonal face rather than a hexagonal face) for $B_8H_8^{4-}$, even among the higher energy $B_8H_8^{4-}$ structures (Figure 2 and Table 2). This also agrees with a prediction by Lee using second moment scaled Hückel theory[22] that a ni-8-⟨VI⟩ structure for $B_8H_8^{4-}$ is favored over a ni-8-⟨V⟩ structure by ~60 kcal/mol.

No minima could be found for a $B_8H_8^{6-}$ cluster. In all instances the cluster dissociated into smaller fragments, presumably because of the high charge confined to a relatively small volume in $B_8H_8^{6-}$.

3.2. 11-Vertex Boranes. The lowest energy structure, **24-1**, computed for $B_{11}H_{11}^{2-}$ (Figure 3 and Table 3) is the C_{2v} most-spherical 11-vertex deltahedron. This polyhedron,

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Table 3. Optimized Structures for $B_{11}H_{11}^{2-}$

structure	rel energy	symmetry	description
24-1	0.0	C_{2v}	edge-coalesced icosahedron ($v_6 = 1$, $v_4 = 2$)
24-2T	38.0	C_{5v}	ni-11-⟨V⟩ structure (one pentagonal face)
24-3	43.3	C_{2v}	alternative 11-vertex deltahedron ($v_6 = 2$, $v_4 = 3$)
24-4	92.5	C_1	3-capped ni-10-⟨V⟩ structure

Table 4. Comparison of the Calculated Geometry Surrounding the Unique Degree 6 Vertex in $B_{11}H_{11}^{2-}$ in This Work with That Found Experimentally for $[Et_3NCH_2Ph][B_{11}H_{11}]$ and $[Li(thp)_2]_2[B_{11}H_{11}]$

structure	v_6-hexagon, Å	x_4/x_2	v_6-spokes, Å	k_4/k_2
calcd for $B_{11}H_{11}^{2-}$	1.67 (x_4), 1.87 (x_2)	0.89	2.03 (k_4), 1.74 (k_2)	1.17
$[Et_3NCH_2Ph][B_{11}H_{11}]$	1.66 (x_4), 1.85 (x_2)	0.90	2.01 (k_4), 1.75 (k_2)	1.15
$[Li(thp)_2]_2B_{11}H_{11}$	1.70 (x_4), 1.79 (x_2)	0.95	2.05 (k_4), 1.61 (k_2)	1.27

which is found experimentally[23] in $B_{11}H_{11}^{2-}$ and isoelectronic carboranes, is commonly called an "edge-coalesced icosahedron", since it is generated from an icosahedron by bringing two vertices together along the edge connecting them until they coalesce at the midpoint of that edge.

The dimensions of the edge-coalesced icosahedron calculated for $B_{11}H_{11}^{2-}$ in this work are very close to those found experimentally[23] in the salts $[Et_3NCH_2Ph][B_{11}H_{11}]$ and $[Li(thp)_2]_2[B_{11}H_{11}]$ (Table 4 and Figure 4), with the agreement being the closest (±0.02 Å) for the tetraalkylammonium salt. This is in accord with the expectation that a tetraalkylammonium ion interacts more weakly with the $B_{11}H_{11}^{2-}$ anion than with a lightly complexed lithium ion in $Li(thp)_2^{+}$.

Our previous papers on germanium clusters[1−3,5] have depicted their bonding molecular orbitals (MOs) using the terminology of tensor surface harmonic theory.[24−28] The relatively low symmetry (C_{2v}) of the lowest energy $B_{11}H_{11}^{2-}$ isomer, **24-1**, makes the shapes of the bonding MOs less distinctive, owing to the increased possibility of mixing orbitals corresponding to the same irreducible representation when the symmetry is lowered. Note, for example, that the C_{2v} point group of $B_{11}H_{11}^{2-}$ does not have any degenerate irreducible representations,[29] so that any degeneracies in the MO energies of $B_{11}H_{11}^{2-}$ must be coincidental.

It is instructive to compare the distribution of the energy parameters of the lowest lying MOs of $B_{11}H_{11}^{2-}$ (**24-1**) with those of the MOs of the highly symmetrical icosahedral $B_{12}H_{12}^{2-}$ (Figure 5). In icosahedral $B_{12}H_{12}^{2-}$, the $1 + 3 + 5 + 7 + 9 = 25$ distribution of the MOs arising from the S, P, D, F, and G spherical harmonics, respectively, can clearly be recognized (see color coded Figure 5).[30] If the relative energies of the bonding molecular orbitals in $B_{12}H_{12}^{2-}$ are used as a basis for crude spherical harmonic assignments in $B_{11}H_{11}^{2-}$, the bonding MOs of $B_{11}H_{11}^{2-}$ follow a $1 + 3 + 5 + 6 + 8 = 23$ orbital pattern (Figure 5). Thus, in going from icosahedral $B_{12}H_{12}^{2-}$ to C_{2v} $B_{11}H_{11}^{2-}$, one F and one G bonding MO is lost. Of course, this analysis is necessarily crude since it does not consider mixing of the $B_{11}H_{11}^{2-}$ MOs, particularly among the higher lying MOs corresponding to the same irreducible representation.

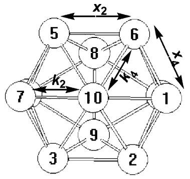

Figure 4. Diagram of the v_6-hexagon edges x_4 and x_2 and the v_6-spoke edges k_4 and k_2 surrounding the unique degree 6 vertex in the edge-coalesced icosahedron.

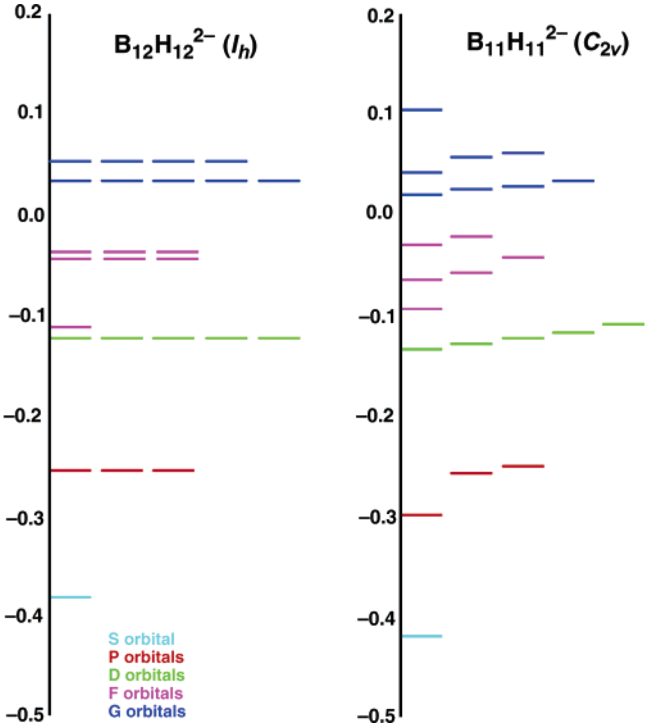

Figure 5. Comparison of the computed energies of the bonding MOs in icosahedral (I_h) $B_{12}H_{12}^{2-}$ and C_{2v} $B_{11}H_{11}^{2-}$ (**24-1** in Figure 3). (See Figure S1 in the Supporting Information for the actual shapes of these orbitals.)

The following additional structures for $B_{11}H_{11}^{2-}$ have also been found at much higher energies than the global minimum, **24-1** (Figure 3 and Table 3): (a) The triplet C_{5v} nido structure **24-2T** with an open pentagonal face is +38.0 kcal/mol above the global minimum, **24-1**. This structure can formally be derived from a nido $B_{11}H_{11}^{4-}$ by a two-electron oxidation that removes exactly half of the electrons from a doubly degenerate highest occupied molecular orbital, leading to a triplet state. This situation is exactly analogous to that discussed above for the triplet square antiprismatic structure **20-6T** for $B_8H_8^{4-}$. (b) A less spherical C_{2v} 11-vertex deltahedron **24-3** with two degree 6 and three degree 4 vertices is +43.3 kcal/mol above the global minimum, **24-1**. This structure could have similar skeletal bonding to the

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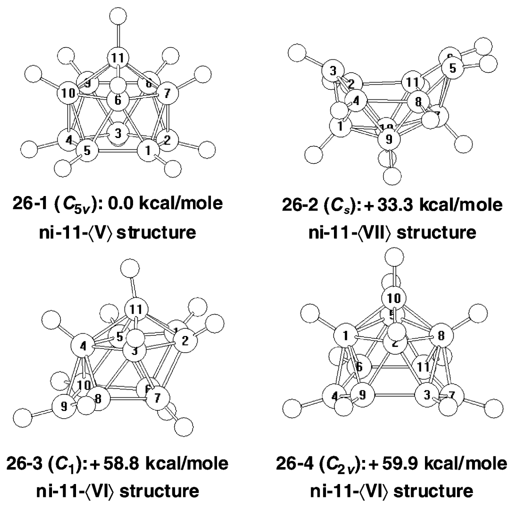


26-1 (C_{5v}): 0.0 kcal/mole ni-11-⟨V⟩ structure

26-2 (C_s): +33.3 kcal/mole ni-11-⟨VII⟩ structure

26-3 (C_1): +58.8 kcal/mole ni-11-⟨VI⟩ structure

26-4 (C_{2v}): +59.9 kcal/mole ni-11-⟨VI⟩ structure

Figure 6. Optimized structures for $B_{11}H_{11}^{4-}$.

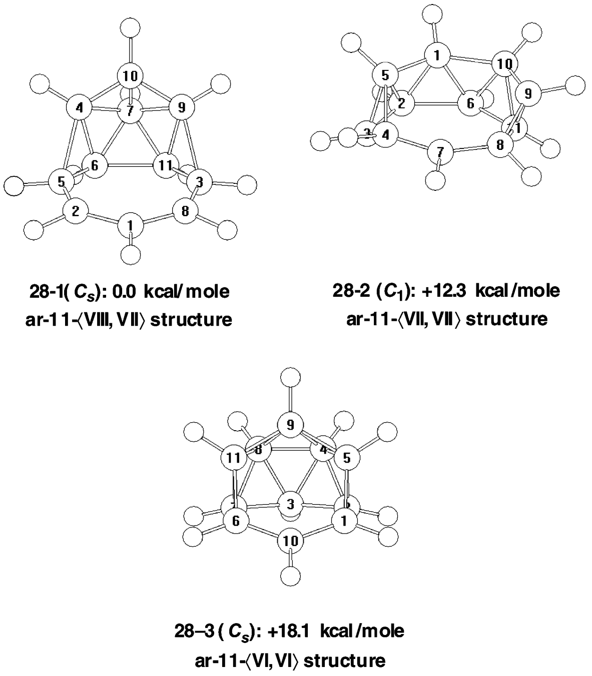
Table 5. Optimized Structures for $B_{11}H_{11}^{4-}$

structure	rel energy	symmetry	description
26-1	0.0	C_{5v}	ni-11-⟨V⟩ structure (one pentagonal face)
26-2	33.3	C_s	ni-11-⟨VII⟩ structure (one heptagonal face)
26-3	58.8	C_1	ni-11-⟨VI⟩ structure (one hexagonal face)
26-4	59.9	C_{2v}	ni-11-⟨VI⟩ structure (one hexagonal face)

lower energy deltahedral structure **24-1** and, thus, also conforms to the Wade−Mingos rules[7−10] with (2)(11) + 2 = 24 skeletal electrons. (c) A very high energy (+92.5 kcal/mol above **24-1**), low symmetry (C_1) structure, **24-4**, is derived from a nido 10-vertex structure with a pentagonal open face by capping one of the triangular faces. It also conforms to the Wade−Mingos rules in having 24 skeletal electrons corresponding to the underlying nido 10-vertex structure.

The global minimum computed for Ge_{11}^{2-} in our previous work[6] is a prolate (elongated) C_{2v} structure with two quadrilateral faces obtained by a minor distortion of a D_{3h} pentacapped trigonal prism. For Ge_{11}^{2-}, this structure was found to be 5.2 kcal/mol below the edge-coalesced icosahedron predicted by the Wade−Mingos rules.[7−10] However, an attempt to optimize a related structure for $B_{11}H_{11}^{2-}$ starting from the D_{3h} pentacapped trigonal prism led, instead, only to the edge-coalesced icosahedron global minimum, **24-1**.

The lowest energy structure found for $B_{11}H_{11}^{4-}$ (Table 5 and Figure 6) is the C_{5v} nido ni-11-⟨V⟩ structure **26-1** with an open pentagonal face analogous to the isoelectronic $C_2B_9H_{11}^{2-}$ ligand found in transition metal chemistry[31,32] as well as the triplet structure **24-2T** computed for $B_{11}H_{11}^{2-}$ discussed above. All of the higher energy structures found for $B_{11}H_{11}^{4-}$ are also nido structures, albeit with different hole sizes and vertex arrangements, and, thus, consistent with the Wade−Mingos[7−10] prediction of nido structures for $B_{11}H_{11}^{4-}$. Thus, the C_s structure **26-2** at +33.3 kcal/mol has a heptagonal open face, whereas the still higher energy structures **26-3** and **26-4** at about +59 kcal/mol have hexagonal open faces but different arrangements of the vertex atoms.



28-1(C_s): 0.0 kcal/mole ar-11-⟨VIII, VII⟩ structure

28-2 (C_1): +12.3 kcal/mole ar-11-⟨VII, VII⟩ structure

28–3 (C_s): +18.1 kcal/mole ar-11-⟨VI, VI⟩ structure

Figure 7. Optimized structures for $B_{11}H_{11}^{6-}$.

Table 6. Optimized Structures for $B_{11}H_{11}^{6-}$

structure	rel energy	symmetry	description
28-1	0.0	C_s	ar-11-⟨VIII,VII⟩ structure (one octagonal, one heptagonal face)
28-2	12.3	C_1	ar-11-⟨VII,VII⟩ structure (two heptagonal faces)
28-3	18.1	C_s	ar-11-⟨VI,VI⟩ structure (two hexagonal faces)

Three minima within a 20 kcal/mol range were found for $B_{11}H_{11}^{6-}$ (Table 6 and Figure 7). All have the two open faces (i.e., nontriangular faces) required for the observed arachno $2n + 6 = 28$ skeletal electron count in accord with the Wade−Mingos rules.[7−10] The open faces in the lowest energy $B_{11}H_{11}^{6-}$ structure, **28-1** (Figure 7), are a heptagon and an octagon. In the next higher energy $B_{11}H_{11}^{6-}$ structure, **28-2**, at +12.3 kcal/mol, the two open faces are heptagons, whereas a $B_{11}H_{11}^{6-}$ structure with two hexagonal faces, **28-3**, lies at the still higher energy of +18.1 kcal/mol.

4. Summary

The most obvious thing about the $B_nH_n^z$ ($n = 8$ and 11, $z = -2$, -4, and -6) clusters relative to the corresponding Ge_n^z clusters is the much larger energy difference between the global minima and other higher energy boranes. Furthermore, for both $B_8H_8^{2-}$ and $B_{11}H_{11}^{2-}$, the lowest energy computed structures are the corresponding experimentally observed most spherical deltahedra predicted by the Wade−Mingos rules, namely the D_{2d} bisdisphenoid and the C_{2v} edge-coalesced icosahedron, respectively. Only in the case of $B_8H_8^{2-}$ is there a second structure close (+2.6 kcal/mol) to the D_{2d} bisdisphenoid global minimum, namely the C_{2v}

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bicapped trigonal prism, corresponding to the square intermediate in a single diamond−square−diamond process that can lead to the experimentally observed room temperature fluxionality of $B_8H_8^{2-}$. Stable borane structures with 3-fold symmetry (e.g., D_{3h}, C_{3v}, etc.) are not found for boranes with 8- and 11-vertices in contrast to the corresponding germanium clusters, where stable structures derived from the D_{3d} bicapped octahedron and D_{3h} pentacapped trigonal prism are found for the 8- and 11-vertex systems, respectively.

The lowest energy structures found for the electron-rich boranes $B_8H_8^{4-}$ and $B_{11}H_{11}^{4-}$ are nido polyhedra derived from a closo deltahedron by removal of a relatively high degree vertex, as predicted by the Wade−Mingos rules. They relate to isoelectronic species found experimentally, e.g., B_8H_{12} and $R_4C_4B_4H_4$ for $B_8H_8^{4-}$ and $C_2B_9H_{11}^{2-}$ for $B_{11}H_{11}^{4-}$. Three structures were found for the electron-rich $B_{11}H_{11}^{6-}$ exhibiting arachno type geometry and having two open faces (hexagons, heptagons, and/or octagons), in accord with the Wade−Mingos rules.

The structural differences between isoelectronic borane and bare germanium clusters observed in our work suggest a significant, but not fully recognized, role of the external hydrogen atoms in the borane clusters. Thus, the external hydrogen atoms in the boranes require one of the four orbitals of the sp^3 manifolds of the boron vertices, so that each boron vertex can only contribute three orbitals to the skeletal (internal) bonding of the polyhedral cluster. However, the lack of external groups in the isoelectronic bare germanium clusters can make the fourth orbital of the sp^3 manifolds of some germanium atoms also available for skeletal bonding, particularly at vertices of high degree. In this connection, an NBO analysis[33] of the molecular orbitals in the T_d tetracapped tetrahedral Ge_8^{2-} anion shows that the occupation of the “lone pair” (LP) orbitals of the germanium atoms at the degree 6 vertices (i.e., those forming the inner tetrahedron) drops to 0.686, as a result of a high degree of delocalization into the skeletal antibonding orbitals. Such involvement of the lone pair orbitals can lead to violation of the Wade−Mingos rules for the bare germanium clusters, so that in some cases their lowest energy structures exhibit different polyhedra than the corresponding boranes.

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Supporting Information Available: B−B and B−H connectivities (Tables S1−S5); lowest lying MOs for two isomers of $B_{11}H_{11}^{2-}$ (Figures S1 and S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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